

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 4/10, 4/14		A1	(11) International Publication Number: WO 97/47661 (43) International Publication Date: 18 December 1997 (18.12.97)
(21) International Application Number: PCT/GB97/01589 (22) International Filing Date: 12 June 1997 (12.06.97) (30) Priority Data: 9612265.0 12 June 1996 (12.06.96) GB 9707024.7 7 April 1997 (07.04.97) GB (71) Applicant (for all designated States except US): UNIVERSITY OF WARWICK [GB/GB]; Gibbet Hill Road, Coventry CV4 7AL (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): HADDLETON, David, Mark [GB/GB]; 3 Whitehead Drive, Kenilworth CV8 2TP (GB). (74) Agent: DEMPSTER, Benjamin, John, Naftel; Withers & Rogers, 4 Dyer's Buildings, Holborn, London EC1N 2JT (GB).			(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERISATION CATALYST AND PROCESS			
(57) Abstract <p>A first aspect of the invention provides a catalyst for addition polymerisation of olefinically unsaturated monomers comprising: a) a first compound MY where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand, Y is a monovalent, divalent or polyvalent counterion; b) an initiator compound comprising a homolytically breakable bond with a halogen atom; and c) an organodiimine, where at least one of the nitrogens of the diimine is not part of an aromatic ring; a second aspect of the invention provides a catalyst for addition polymerisation of olefinically unsaturated monomers comprising: d) a first component of the Formula $[ML]^{n+} A^{n-}$ where M = a transition metal of low valency state, L = an organodiimine where at least one of the nitrogens of the diimine is not part of an aromatic ring, A = an anion, n = an integer of 1 to 3, m = an integer of 1 or 2; e) an initiator compound comprising a homolytically breakable bond with a halogen atom. Preferably, the organodiimine is a 1,4-diaza-1,3- butadiene, a pyridine carbaldehyde imine, an oxazolidone or a quinoline carbaldehyde. Processes for using the catalysts are also disclosed.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

POLYMERISATION CATALYST AND PROCESS

The present invention relates to a process for the atom transfer
polymerisation of olefinically unsaturated monomers in which molecular
weight control is achieved by the presence of certain transition metal,
5 especially copper. diimine complexes.

It is desirable to be able to produce high molecular weight polymers with
a low molecular weight distribution by catalysed addition polymerisation,
10 in particular of vinylic monomers. Hitherto this has been achieved by
polymerising via ionic processes typically in the presence of
organometallics such as alkyl lithium's which are sensitive as regards
reaction with water and other protic species. As such monomers
containing functional groups are not readily polymerised. The use of ionic
15 systems also precludes the use of solvents which contain protic groups
and/or impurities resulting in very stringent reaction conditions and
reagent purity being employed.

More recently radical polymerisation based on the combination of
20 a transition metal halide and alkyl halide have been utilised. For example
Matyjasewski (Macromolecules (1995), vol 28. pages 7901-7910 and

WO96/30421) has described the use of CuX (where X=Cl, Br) in conjunction with bipyridine and an alkyl halide to give polymers of narrow molecular weight distribution and controlled molecular weight. This system suffers from the disadvantage that the copper catalyst is only partially soluble in the system and thus a heterogeneous polymerisation ensues. The level of catalyst which is active in solution is thus difficult to determine. Percec (Macromolecules, (1995), vol. 28, page 1995) has extended Matyjasewski's work by utilising arenesulphonyl chlorides to replace alkyl chlorides, again this results in heterogeneous polymerisation. Sawamoto (Macromolecules, (1995), vol. 28, page 1721 and Macromolecules, (1997), vol. 30, page 2244) has also utilised a ruthenium based system for similar polymerisation of methacrylates. This system requires activation of monomer by aluminium alkyl, itself sensitive to reaction with protic species which is an inherent disadvantage. These systems have been described as proceeding via a free radical mechanism which suffers from the problem that the rate of termination is > 0 due to normal radical-radical combination and disproportionation.

Surprisingly the inventors have found that the use of diimines such as 1,4-diaza-1,3-butadienes and 2-pyridinecarbaldehyde imines may be used in place of bipyridines. These ligands offer the advantage of homogeneous

polymerisation and thus the level of active catalyst can be accurately controlled. This class of ligand also enables the control of the relative stability of the transition metal valencies, for example, Cu(I) and Cu(II), by altering ancillary substituents and thus gives control over the nature of the products through control over the appropriate chemical equilibrium.

5 Such a system is tolerant to trace impurities, trace levels of O₂ and functional monomers, and may even be conducted in aqueous media.

A further advantage of the system of the invention is that the presence of free-radical inhibitors traditionally used to inhibit polymerisation of commercial monomers in storage, such as 2, 6-di-tert-butyl-4-methylphenol (topanol), increases the rate of reaction of the invention.

10 This means that lengthy purification of commercial monomers to remove such radical inhibitors is not required. Furthermore, this indicates that the system of the invention is not a free-radical process. This is contrary to the Matajaszewski and Sawamoto who show free-radical based systems.

15

Accordingly a first aspect of the invention provides a catalyst for addition polymerisation of olefinically unsaturated monomers, especially vinylic monomers, comprising:

20

- a) a first compound of formula 1



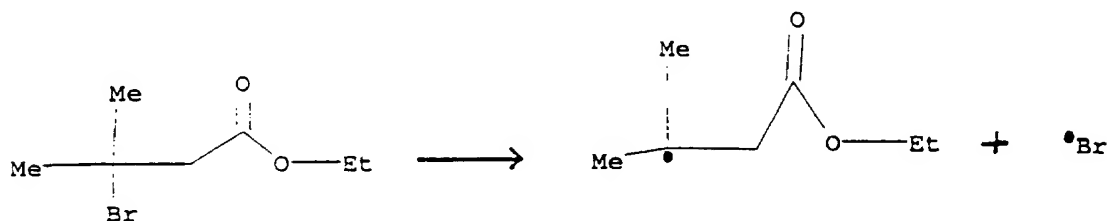
where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion;

- b) an initiator compound comprising a homolytically cleavable bond with a halogen atom;

- c) an organodiimine, where one of the nitrogens of the diimine is not part of an aromatic ring.

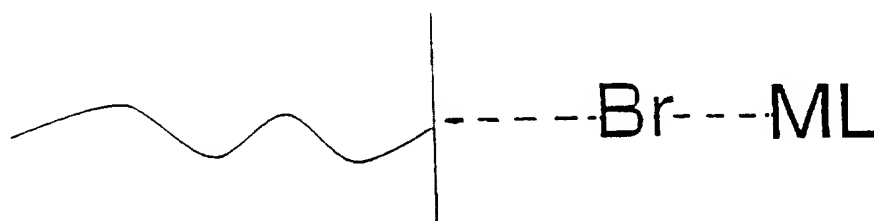
Homolytically cleavable means a bond which breaks without lintegral charge formation on either atom by homolytic fission.

Conventionally this produces a radical on the compound and a halogen atom radical. For example:



However, the increase in the rate of reaction observed by the inventors with free-radical inhibitors indicates that true free-radicals do not appear to be formed using the catalysts of the invention. It is believed

that this occurs in a concerted fashion whereby the monomer is inserted into the bond without formation of a discrete free radical species in the system. That is during propagation this results in the formation at a new carbon-carbon bond and a new carbon-halogen bond without free-radical formation. The mechanism involves bridging halogen atoms such as:



10 where:

ML is a transition metal-diimine complex as defined below.

A "free-radical" is defined as an atom or group of atoms having an unpaired valence electron and which is a separate entity without other interactions.

15

Transitional metals may have different valencies, for example Fe(II) and Fe(III), Cu(I) and Cu(II), a low valency state is the lower of the commonly occurring valencies, i.e. Fe(II) or Cu(I). Hence M in Formula I is preferably Cu(I), Fe(II), Co(II), Ru(II) or Ni(II), most preferably Cu(I).

20

Preferably the co-ordinating ligand is $(\text{CH}_3\text{CN})_4$. Y may be chosen from Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3).

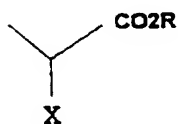
Copper (I) triflate may be, which may be in the form of a commercially available benzene complex $(\text{CF}_3\text{SO}_3\text{Cu})_2\text{C}_6\text{H}_6$. The especially preferred compound used is CuBr.

Preferably the second component (b) is selected from

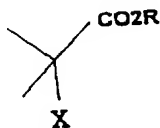
RX

Formula 2

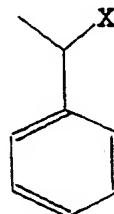
15



Formula 3

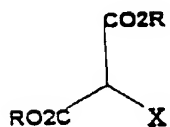


Formula 4

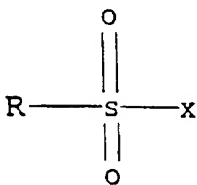


Formula 5

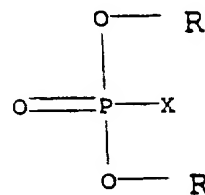
20



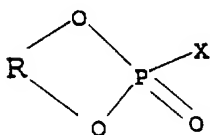
Formula 6



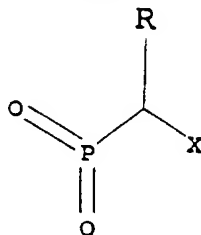
Formula 7



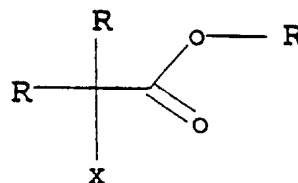
Formula 8



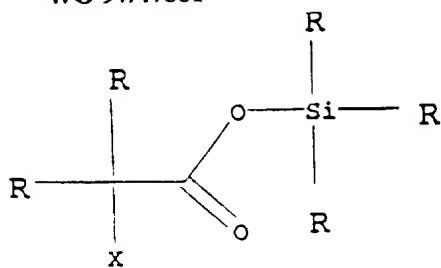
Formula 9



Formula 10



Formula 11



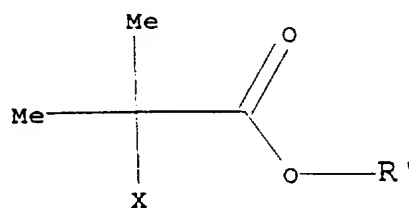
Formula 12

7

5 where R is independently selectable and is selected from straight, branched or cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl or substituted benzyl. Preferably the or each alkyl, hydroxyalkyl or carboxyalkyl contains 1 to 20, especially 1 to 5 carbon atoms.

10 X is a halide, especially I, Br, F or Cl.

The second component (b) may especially be selected from Formulae 13 to 23:



Formula 13

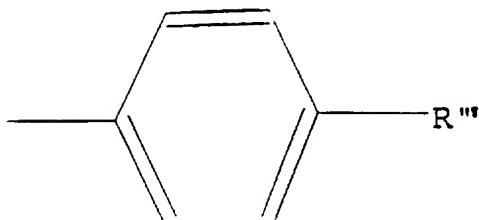
where:

X = Br, I or Cl, preferably Br

R' = -H,

$-(CH_2)_pR''$ (where m is a whole number, preferably $p = 1$ to 20 , more preferably 1 to 10 , most preferably 1 to 5 , $R'' = H, OH, COOH$, halide, NH_2 , SO_3 , CoX - where x is Br, I or C) or:

5

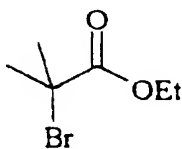


Formula 14

$R''' = -COOH, -COX$ (where X is Br, I, F or Cl), $-OH, -NH_2$ or $-SO_3H$,

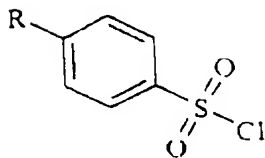
10

especially 2-hydroxyethyl-2'-methyl-2' bromopropionate.



15

Formula 15

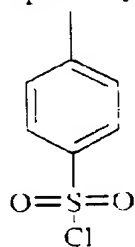


$R = Me, MeO, \text{halogen}.$

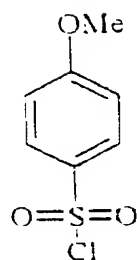
20

Formula 16

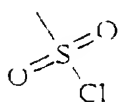
Especially preferred examples of Formula 16 are:



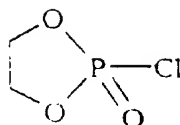
Formula 16A



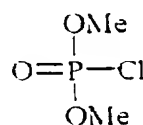
Formula 16B



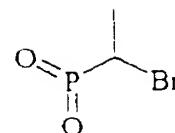
Formula 17



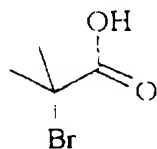
Formula 18



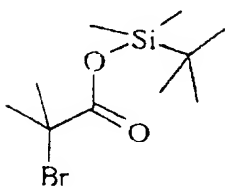
Formula 19



Formula 20

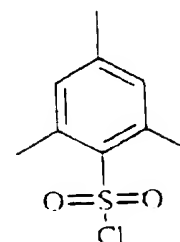


Formula 21



Formula 22

and

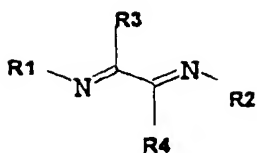


Formula 23

The careful selection of functional alkyl halides allows the production of terminally functionalised polymers. For example, the selection of a hydroxy containing alkyl bromide allows the production of α -hydroxy terminal polymers. This can be achieved without the need of protecting group chemistry.

Component (c) may be a 1,4-diaza-1,3-butadiene

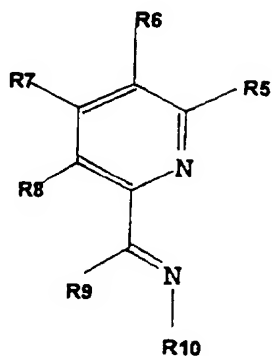
10



5

Formula 24

a 2-pyridinecarbaldehyde imine

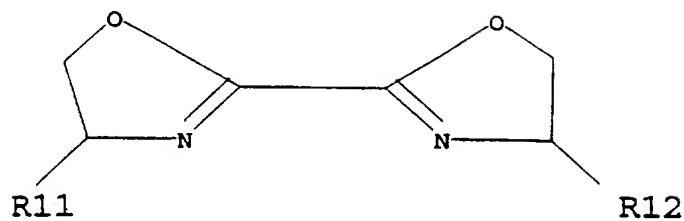


10

Formula 25

An Oxazolidone

15

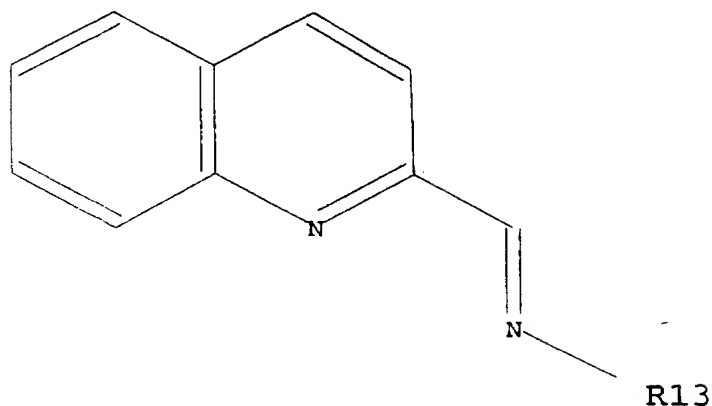


20

Formula 26

or a Quinoline Carbaldehyde

5



10

Formula 27

where R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} may be varied independently and R_1 ,
15 R_2 , R_{10} , R_{11} , R_{12} and R_{13} may be H, straight chain, branched chain or cyclic
saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or phenyl
substituted where substitution is as described for R_4 to R_9), CH_2Ar (where
 Ar = aryl or substituted aryl) or a halogen. Preferably R_1 , R_2 , R_{10} , R_{11} , R_{12}
and R_{13} may be a C_1 to C_{20} alkyl, hydroxyalkyl or carboxyalkyl, in
20 particular C_1 to C_4 alkyl, especially methyl or ethyl, n-propylisopropyl, n-
butyl, sec-butyl, tert butyl, cyclohexyl, 2-ethylhexyl, octyl decyl or lauryl.

R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} may especially be methyl.

R_3 to R_9 may independently be selected from the group described for R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} or additionally OCH_{2n+1} (where n is an integer from 1 to 20), NO_2 , CN or $O=CR$ (where R = alkyl, benzyl $PhCH_2$ or a substituted benzyl, preferably a C_1 to C_{20} alkyl, especially a C_1 to C_4 alkyl).

Furthermore, the compounds may exhibit a chiral centre α to one of the nitrogen groups. This allows the possibility for polymers having different stereochemistry structures to be produced.

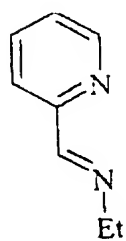
Compounds of general Formula 25 may comprise one or more fused rings on the pyridine group.

One or more adjacent R_1 and R_3 , R_3 and R_4 , R_4 and R_2 , R_{10} and R_9 , R_8 and R_9 , R_8 and R_7 , R_7 and R_6 , R_6 and R_5 groups may be C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norborneyl.

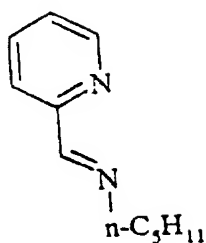
Preferred ligands include:

Preferred ligands include:

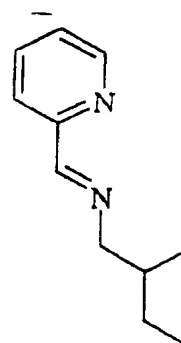
5



Formula 28

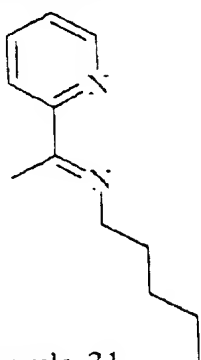


Formula 29

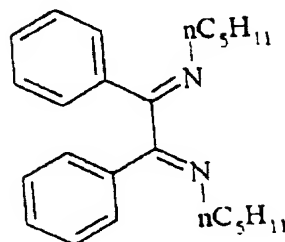


Formula 30

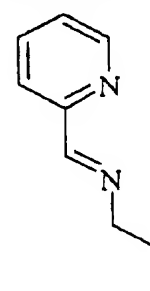
10



Formula 31

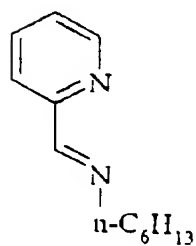


Formula 32

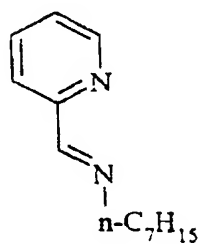


Formula 33

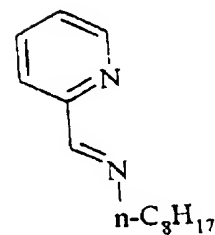
15



Formula 34

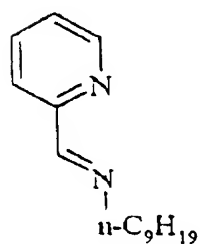


Formula 35

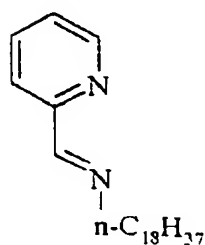


Formula 36

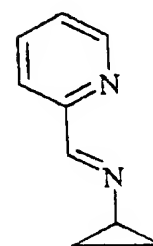
20



Formula 37

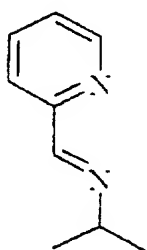


Formula 38

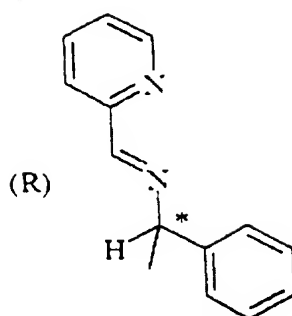


Formula 39

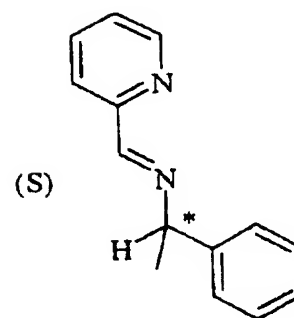
14



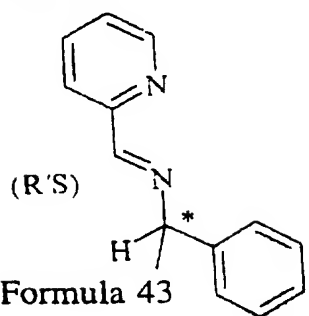
Formula 40



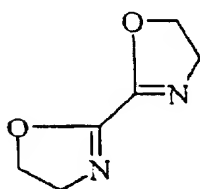
Formula 41



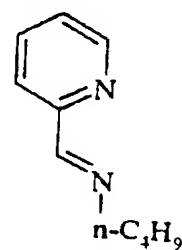
Formula 42



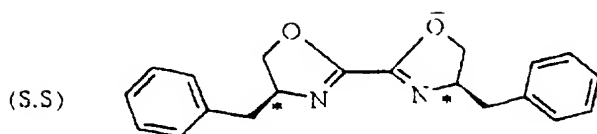
Formula 43



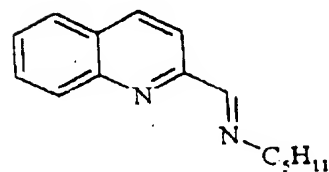
Formula 44



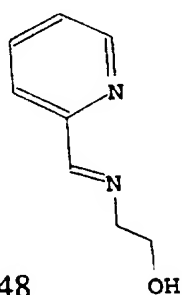
Formula 45



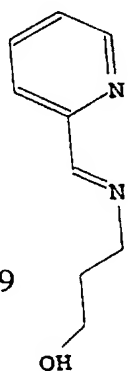
Formula 46



Formula 47



Formula 48

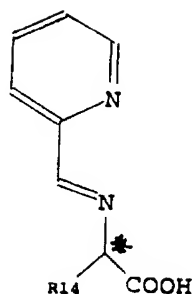


Formula 49

15

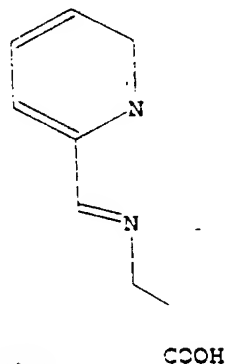
Formula 50

and



5

Formula 51



10

where: * indicates a chiral centre

COOH

R14 = Hydrogen, C₁ to C₁₀ branched chain alkyl, carboxy- or hydroxy- C₁ to C₁₀ alkyl.

15

20

A second aspect of the invention provides a catalyst for addition

polymerisation of olefinically unsaturated monomers, especially vinylic monomers, comprising:

a first component of Formula 51



wherein M = a transitional metal in a low valency state;

L = an organodiimine, where at least one of the nitrogens of the diimine is not part of an aromatic ring,

A = an anion

10 n = a whole integer of 1 to 3

m = an integer of 1 to 2.

(e) An initiator comprising a homolytically cleavable bond with a halogen atom, as previously defined.

15

Preferably M is as previously defined for component (a). L may be a compound according to Formula 24, 25, 26 or 27, as previously defined.

A may be F, Cl, Br, I, NO₃, SO₄ or CuX₂ (where X is a halogen).

20 The preferred initiators (e) are as defined for the first aspect of the invention.

The invention also provides the use of the catalyst according to the first or second aspect of the invention in the addition polymerisation of one or more olefinically unsaturated monomers and the polymerised products of such processes.

5

The components (a), (b) and (c), or (d) and (e) may be used together in any order.

10

The inventors have unexpectedly found that the catalyst will work at a wide variety of temperatures, including room temperature and as low as -15°C. Accordingly, preferably the catalyst is used at a temperature of -20°C to 200°C, especially -20°C to 150°C, 20°C to 130°C, more preferably 90°C.

15

The olefinically unsaturated monomer may be a methacrylic, an acrylate, a styrene, methacrylonitrile or a diene such as butadiene.

20

Examples of olefinically unsaturated monomers that may be polymerised include methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates

including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates; methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene, α -methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula $\text{CH}_2 = \text{C}(\text{Hal})_2$ where each halogen is independently Cl or F; optionally substituted butadienes of the formula $\text{CH}_2 = \text{C}(\text{R}^{15})\text{C}(\text{R}^{15}) = \text{CH}_2$ where R^{15} is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula $\text{CH}_2 = \text{CHSO}_2\text{OM}$ wherein M is Na, K, Li, $\text{N}(\text{R}^{16})_4$ where each R^{16} is independently H or C1 to C10 alkyl, D is COZ, ON, $\text{N}(\text{R}^{16})_2$ or SO_2OZ and Z is H, Li, Na, K or $\text{N}(\text{R}^{16})_4$; acrylamide or derivatives thereof of formula $\text{CH}_2 = \text{CHCON}(\text{R}^{16})_2$ and methacrylamide or derivative thereof of formula $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CON}(\text{R}^{16})_2$. Mixtures of such monomers may be used.

Preferably, the monomers are commercially available and may comprise a free-radical inhibitor such as 2, 6-di-tert-butyl-4-methylphenol or methoxyphenol.

Preferably the co-catalysts are used in the ratios (c):(a) 0.01 to 1000,

preferably 0.1 to 10, and (a):(b) 0.0001 to 1000, preferably 0.1 to 10, where the degree of polymerisation is controlled by the ratio of monomer to (b).

5 Preferably the components of the catalyst of the second aspect of the invention are added at a ratio M:initiator of 3:1 to 1:100.

Preferably the amount of diimine : metal used in the systems is between 100:1 and 1:1, preferably 5:1 to 1:1, more preferably 3:1 to 1:1.

10

The reaction may take place with or without the presence of a solvent. Suitable solvents in which the catalyst, monomer and polymer product are sufficiently soluble for reactions to occur include water, protic and non-protic solvents including propionitrile, hexane, heptane, dimethoxyethane, diethoxyethane, tetrahydrofuran, ethylacetate, diethylether, N,N-
15 dimethylformamide, anisole, acetonitrile, diphenylether, methylisobutyrate, butan-2-one, toluene and xylene. Especially preferred solvents are xylene and toluene, preferably the solvents are used at at least 1% by weight, more preferably at least 10% by weight.

20

Preferably the concentration of monomer in the solvents is 100% to 1%,

preferably 100% to 5%.

The reaction may be undertaken under an inert atmosphere such as nitrogen or argon.

5

The reaction may be carried out in suspension, emulsion, mini-emulsion or in a dispersion.

10

Statistical copolymers may be produced using the catalysts according to the invention. Such copolymers may use 2 or more monomers in a range of ca.0-100% by weight of each of the monomers used.

Block copolymers may also be prepared by sequential addition of monomers to the reaction catalyst.

15

Telechelic polymers, may be produced using catalysts of the invention. For example, a functional initiator such as Formula 21 may be used with transformation of the ω Br group to a functional group such as -OH or -CO₂H via use of a suitable reactant such as sodium azide.

20

Comb and graft copolymers may be produced using the catalysts of the

invention to allow, for example, polymers having functional side chains to be produced, by use of suitable reagents.

Embodiments of the invention will now be described by way of example and with reference to the following figures:

Fig. 1 shows the structure of the ligand 2,6 dimethylanilineDAB;

Fig. 2 shows the crystal structure of the cation obtained by reacting tBuDAB and CuBr together;

Figs. 3 and 4 show Mn dependence on conversion of different monomer initiator ratios for styrene and methylmethacrylate respectively;

Fig. 5 shows Mw/Mn dependence on conversion for bulk polymerisation of styrene at 80°C;

Fig. 6 shows kinetic plots for polymerisation of methylmethacrylate at 90°C;

Fig. 7 shows the reaction scheme for the production of hydroxy terminally functionalised PMMA. (i) Br₂-P, (ii) Ethylene glycol, (iii) CuBr/3/MMA, (iv) benzoyl chloride;

Fig. 8 shows a selected region from ¹H NMR spectra of (a) 3, (b) 4 CH₂-O-groups and -OCH₃ \propto to Br and aromatic protons from benzoyl group;

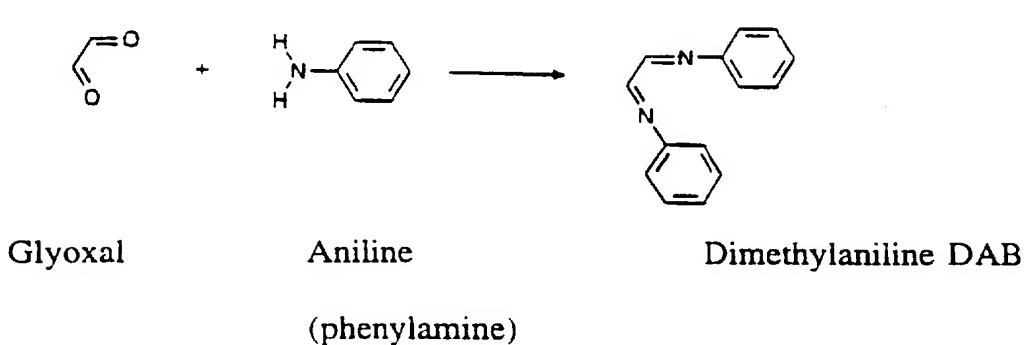
Fig. 9 shows partial MALDI-TOF-MS of 3 between $x = 8$ and 11, peaks correspond to lithium adducts of molecular ions with no observable fragmentation;

Fig. 10 shows a plot showing how Mn from SEC increases with conversion for experiments D-K.

Examples

Synthesis of Ligands

Diazabutadiene (DAB) Ligands

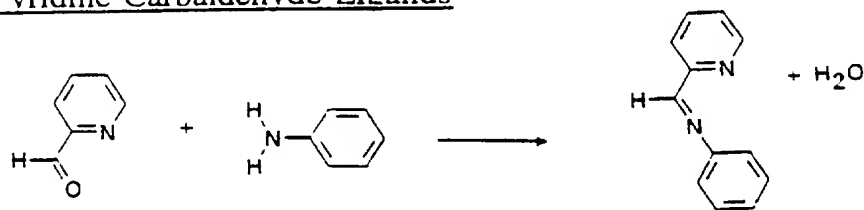


15 To a stirred solution of 40% aqueous glyoxal (0.25 mol) in a conical flask was added the required amine dropwise (0.5 mol). After a period of time a pale yellow solution formed which was taken up with water and filtered. The resulting precipitate was dissolved in diethyl ether and poured over a

20 large excess of magnesium sulphate. The solution was left for twelve hours to remove all the water and the solution was filtered. Ether was

removed on a rotary evaporator then the product recrystallised from ether. TertButyl DAB (tBu DAB) and isoPropyl DAB (iPr DAB) were similarly manufactured using t-butylamine and isopropylamine respectively as the starting amine. Such compounds are superior to 2,2-bipyridine in accepting electron density

Pyridine Carbaldehyde Ligands



2-pyridinecarb-
aldehyde

aniline

aniline PCA

To a stirred solution of pyridine carbaldehyde in ether was added an equimolar quantity of amine. The solution was left for 3 hours then poured over an excess of magnesium sulphate. The solution was filtered and the ether removed on a rotary evaporator. Some ligands formed yellow oils and were purified by distillation under reduced pressure. Solids were purified by recrystallisation from ether.

tBu PCA, iPr PCA, nButyl PCA (nBu PCA), Dimethylaniline PCA,

Diisopropylaniline PCA and methoxyaniline PCA were also made by reacting $t\text{-BuNH}_2$, $i\text{-PrNH}_2$, $n\text{-BuNH}_2$, 2,6-dimethylaniline, 2,6-diisoproxylaniline and 4-methoxyaniline, respectively as the amine.

Characterisation of Ligands

Ligands have been initially characterised by NMR and EI/CI mass spectrometry. Mass spec data is tabulated below.

DIAZABUTIENE (DAB) LIGANDS

Structure	RMM	M/Z
tBu DAB	168	166
iPr DAB	140	141
Dimethylaniline DAB	262	249

PYRIDINE CARBALDEHYDE

(PCA) LIGANDS

Structure	RMM	M/Z
tBu PCA	162	163
iPr PCA	149	149
nBu PCA	162	163
Aniline PCA	182	182
Dimethylaniline PCA	212	209
Diisopropylaniline PCA	268	223
Methoxyaniline PCA	197	211

A crystal structure has been obtained of the ligand 2, 6 dimethylaniline DAB (Fig. 1). This shows a E configuration of double bonds which must fold around the metal centre to form the catalyst.

Synthesis of Catalysts

To a solution of ligand (in acetone) in a schlenk was added copper bromide . chloride or $\text{Cu}(\text{CH}_3\text{CN})\text{BF}_4$ under nitrogen. The solution was filtered by cannular and placed in a freezer. Solvent was removed by filtration and the crystals examined by FAB mass spectrometry. Catalysts were synthesised with equimolar quantities of ligand and anion or excess ligand (2:1). Both experiments resulted in the detection of a peak corresponding to CuL_2 .

L = ligand.

Ligand	Ligand : anion	Anion	Mass spectrometry data M/Z			
			CuL	CuL ₂	Cu ₂ L ₂ Cl ₂	Cu ₂ L ₂ Cl ₄
tBuDAB	1:1	Br	231	399		
tBuDAB	1:1	BF ₄	231	399		
tBuDAB	2:1	Br	231	399		
tBuDAB	1:1	Cl	-	399	499	597
iPrDAB	1:1	Br	203	343		
tBuPCA	1:1	Br	225	387		
tBuPCA	1:1	BF ₄	225	387		
tBuPCA	1:1	Cl	-	387		
Bipy	1:1	Br	300	456		
Bipy	1:1	BF ₄	219	375		
Bipy	2:1	BF ₄	219	375		
Bipy	1:1	Cl	-	375		

Bipy (Bipyridyl) is included as a comparison.

A crystal structure has been obtained for the reaction of tBu DAB and CuBr indicating a tetrahedral intermediate (Fig. 2).

Polymer Synthesis

The catalysts were used to control the propagation of styrene and methylmethacrylate.

5

All polymerisations were performed with excess ligand [L]:[Cu] 3:1 and the catalyst is synthesised in situ.

General method for polymerisation of methvlmethacrylvlate

10

To a Schlenk to be purged with nitrogen was added 0.54mls ethyl 2-bromo-isobutyrate (0.00372 mols) in 10mls methylmethacrylate (0.0935 mols). The desired ligand was then added (0.01122 mols) and the entire solution freeze pump thaw degassed. 0.536g copper bromide (0.00374

15 mols) was then added whilst stirring. When the solution turned deep red indicating formulation of the catalyst the schlenk was immersed in an oil bath at 90°C.

Polymerisation results

All polymerisations are based on the following mole ratios.

Monomer : Initiator : Copper X : Ligand

100 : 1 : 1 : 3

Copper X = catalyst based on copper.

Styrene (Sty) was initiated with 1-phenylethyl bromide or chlorine.

Methylmethacrylate (MMA) was initiated with ethyl-2-bromo isobutyrate.

ligand	mon.	X	t/hrs	T/C	Mn	Mw	PDi	Conv%
tBuDAB	STY	Br	24	110	2.173	4.438	2	11
iPrDAB	STY	Br	24	110	1.975	72.587	38	5
dimethylanilineDAB	STY	Br	24	110	467	4.156	9	80
tBuPCA	STY	Br	24	110	338	1.110	3.2	1
anilinePCA	STY	Br	24	110	6.458	22.376	3.5	41
dimethylaniline	STY	Br	24	110	3.017	9.167	3	68
tBuPCA	STY	Cl	20	130	42.551	102.776	2.45	20
nBuPCA	STY	Cl	3	130	6.951	22.571	3.25	40
iPrPCA	STY	Cl	20	130	15.607	41.125	2.64	33
anilinePCA	STY	Br	20	110	6.458	22.376	4	41
dimethylanilinePCA	STY	Br	20	110	3.017	9.167	3	68
isopropylanilinePCA	STY	Br	20	130	3.700	10.074	2.72	61
methoxyanilinePCA	STY	Br	20	130	9.723	24.772	2.5	69
anilinePCA	MMA	Br	18	110	477	4.600	9.6	2
dimethylanilinePCA	MMA	Br	18	110	6.293	12.210	1.94	68
nBuPCA	MMA	Br	4	100	10.251	12.273	1.2	95
nBuPCA	MMA	Br	1	130	7.376	12.422	1.68	-
nBuPCA	STY	Br	40	80	5.492	7.313	1.33	43
nBuPCA	STY	Br	20	80	6.343	9.533	1.5	39

Polymerisation with tBuDAB

t-BuDAB was also investigated in more detail using different ratios of Ligand (L), Initiator (I) and catalyst (Cu).

5

Styrene at 100°C

	<u>L:I</u>	<u>Cu:I</u>	<u>Mn</u>	<u>PDI</u>	<u>%Conv.</u>
	3	1	2173	2.0	11
10	3	20	2603	4.0	7
	3	100	2169	5.8	8
	1	1	2400	3.6	9
	1	100	8042	14	7

15

MMA

(100°C)

3	1	2020	4.1	Low
---	---	------	-----	-----

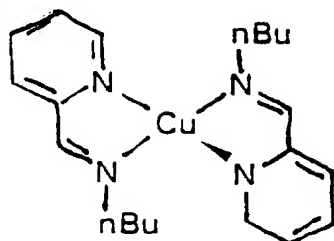
This shows that PDI may be controlled by varying the ratio of L:I and/or

20

Cu:I.

Polymerisations with nBuPCA

The most successful ligand was nBuPCA which will form the following copper (I) structure:



This catalyst has been used to obtain kinetic data for the polymerisation of both styrene and methylmethacrylate. Temperature control is important to prevent termination leading to tailing of the resulting MW distribution. If termination is prevented then polydispersity will decrease with time. Mn conversion plots have been obtained at different monomer to initiator ratios.

Figs. 3 and 4 show Mn dependence on conversion at different monomer:initiator for styrene and methylmethacrylate at 80°C.

Fig. 5 shows M_w/M_n dependence on conversion for bulk polymerisation of styrene at 80°C.

Fig. 6 shows kinetic plots for the polymerisation of methylmethacrylate at 90°C.

Synthesis of Block Co-polymers

This was investigated using methylmethacrylate, benzylmethacrylate (BzMA) and 2 hydroxyethylmethacrylate (HEMA) the results of which are shown in the table below:

TABLE B

BLOCK ONE				BLOCK TWO				
Mon.	Mn	Mw	PDI	Mon.	Mn	Mw	PDI	% MMA
MMA	2,469	2,965	1.2	MMA	5,599	7,337	1.31	100
MMA	2,469	2,965	1.2	BzMA	4,908	6,500	1.32	70
MMA	2,499	3,431	1.37	BzMA	5,934	10,749	1.81	54
MMA	2,499	3,431	1.37	HEMA	3,298	5,544	1.68	70

Statistical Copolymers

An example of a statistical copolymer was produced using a compound of Formula 16B as initiator and a compound of Formula 45 as the ligand.

1g of 2-hydroxyethyl methacrylate with 9.36g of MMA (I. e. 7.7. mole%)
was polymerised with the following results:

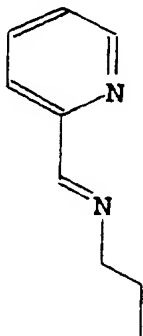
Initiator	Ligand	Amount ligand/ mL	Solvent (conc wt%)	Amt. CuBr/g	Amt. Initiator /g	Temp. °C	Time mins.
16B	45	0.37	33.3	0.13	0.16	90	2760

Results:

Mn	PDI	% HEMA (NMR)
14764	1.21	4.5

Further experimentation

Further experimentation was also carried out using ligands of Formula 33.



Formula 33

This was synthesised as follows:

30mls of diethylether was placed in a conical flask. 1.78mls of 2-pyridine
carbaldehyde (2.00g, 1.867×10^{-2} moles) were added prior to 1.54mls or

propylamine (1.11g, 1.873×10^{-2} moles). The reaction mixture immediately turns yellow. The mixture was stored for 10 minutes at room temperature prior to the addition of magnesium sulphate and stirring for a further 30 minutes. The reaction mixture was filtered and the volatiles removed under reduced pressure. The product is isolated as a yellow oil.

Polymerisation

0.688g of copper (I) bromide (98% Aldrich) (4.796×10^{-4} moles) were added to 10mls of methylmethacrylate purified by passage down a column containing basic alumina and 3A sieves under nitrogen (9.349×10^{-2} moles) in 20 mls of xylene (deoxygenated by 3 freeze-pump-thaw cycles and dried over 3A sieves for 12 hours). 0.2136g of A (1.44×10^{-3} moles) were added over 2 minutes with stirring at room temperature to give a homogenous deep red/brown solution. 0.07mls of ethyl 2-bromoisobutyrate (0.0924g , 4.73×10^{-4} moles) were added and the reaction mixture heated to 90°C for 485 minutes. Samples were taken at intervals and analysed for Mn and conversion, see table. After 485 minutes poly(methylmethacrylate) was isolated by precipitation into methanol in 78.6% yield with $\text{Mn} = 7020$ and $\text{PDI} (\text{Mw}/\text{Mn}) = 1.27$.

34

	<u>TIME</u>	<u>% CONVERSION</u>	<u>Mn</u>	<u>PDI</u>
	120	16.47	2376	1.28
	240	52.69	5249	1.22
	300	61.02	6232	1.18
5	360	67.56	6742	1.21
	485	78.56	7020	1.27

The Production of α -hydroxy terminally functionalised PMMA

10 The initiator, ethyl-2-bromoisobutyrate was replaced with hydroxy containing alkyl bromide so as to produce α -hydroxy terminally functionalised PMMA without the need to employ protecting group chemistry.

15 Ligands of Formula 33 were used in the polymerisation process.

2-hydroxyethyl-2'-methyl-2'bromopropionate was prepared as shown in Fig. 7.

20 The conditions used in steps (1) and (ii) was as follows:

0.25g of red phosphorous (8.06×10^{-3} mol) were added to 35.4ml (0.338

mol) of isobutyryl chloride. The mixture was placed under gentle reflux and 20ml of bromine (0.338 mol) were added slowly over 8 hours. The mixture was refluxed for a further 4 hours and the crude reaction mixture added slowly to 350ml of anhydrous ethylene glycol (6.27 mol). The reaction mixture was refluxed for 4 hours, filtered into 500ml of distilled water and the product extracted into chloroform. After washing with water and sodium hydrogen carbonate and drying over magnesium sulphate the product was isolated as a colourless liquid after the removal of solvent and vacuum distillation at 64.5°C and 0.1 Torr. ¹H NMR (CDCl₃, 373 K, 250.13 MHz) δ = 4.30 (t, J 9.6 Hz, 2H), 3.85 (t, J 9.6 Hz, 2H) 1.94 s, 6H), ¹³C (¹H) NMR (CDCl₃, 373 K, 100.6 mHz) δ = 171.83, 67.30, 60.70, 55.72, 30.59, IR (NaCl, film) 3436 (br), 2977, 1736 (s), 1464, 1391, 1372, 1278, 1168, 1112, 1080, 1023, 950, 644, EI MS: 213, 211 (mass peaks), 169, 167, 151, 149, 123, 121. The typical polymerisation procedure used (steps iii and iv) was as follows: 0.1376 of copper(1)bromide (98%, 9.6 x 10⁻⁴ mol) were added to 40ml of xylene and 20ml of methyl methacrylate (0.187 mol). 0.4272g of 2 (2.89 x 10⁻³ mol) were added and the mixture deoxygenated by one freeze-pump-thaw cycle prior to the addition of 0.2029g of 3 (9.61 x 10⁻⁴) mol at room temperature. The deep red solution was heated at 90°C for 70 minutes. The final product was isolated by precipitation into hexanes.

Atom transfer radical polymerisation of MMA using 3 as initiator in conjunction with 2 and CuBr was carried out at 90°C in xylene [MMA]:[3] = 20:1, [ligand]:[CuBr]:[3] = 3:1:1 to give PMMA of structure 4. Polymerisation was stopped at low conversion. 7.65%, after 70 minutes, so as to reduce the amount of termination by radical-radical reactions. reaction A. ¹H NMR data (Fig. 8), clearly shows the presence of the hydroxyethyl ester group, originating from 2 and the methoxy α to the bromo group at the propagating end at δ 4.28, 3.82 and 3.74 respectively. The number average molecular mass, M_n , can be calculated directly from NMR which gives a value of 2430 which compares excellently with that obtained from size exclusion chromatography against PMMA standards of 2320, PDI = 1.12 (when precipitated into hexanes M_n - 2960, PDI = 1.12). This excellent agreement indicates that the product has structure 4. This is confirmed by matrix-assisted laser desorption-ionisation time of flight mass spectrometry, Fig. 9. We see one series of peaks in the MALDI-TOF-MS indicating only one predominant structure i.e. 4. For example, the peaks at m/z 1319.0 and 1419.2 correspond to lithium adducts of 4 where $x = 10$ and 11 respectively, calculated m/z 1318.3 and 1418.4. The narrow PDI of 4 is indicative of $k(\text{propagation}) \gg k(\text{termination})$ i.e. pseudo living polymerisation. Control over M_n and PDI is obviously not affected detrimentally by the presence of primary

alcohol group present in the initiator, which might have been expected to complicate the reaction by coordination to the copper catalyst. Indeed the PDI is narrower and the rate of polymerisation faster with 3 than that obtained using a non functional initiator. This is currently under investigation. Thus, controlled polymerisation with the copper complex as catalyst can be utilised to give PMMA or structure 4 as the only detectable product under these conditions. The hydroxy group can be further reacted with benzoyl chloride to give 5 quantitatively.

The terminal benzoyl group of 5 is observed by ^1H NMR, Fig. 8(c) and is detected by SEC with UV detection at 200 nm, 4 shows no absorption at this wavelength. MALDI TOF shows a new series of peaks corresponding to 5 e.g. peaks are now observed at m/z 1423.0 and 1522.8 for $x = 10$ and 11, calculated m/z 1422.3 and 1522.4; this reaction is quantitative and no peaks from residual 4 are observed. When the reaction is carried out at a higher [MMA]:[3] ratio for 120 minutes a higher molecular weight polymer is produced, $M_n = 4540$, $PDI = 1.22$, as expected, reactions B and C. Again analysis shows terminal hydroxy functionality.

Living or pseudo living polymerisations have a low rate of termination relative to rate of propagation. This is demonstrated by following a

reaction with time. reactions D-K; L is the final product from this reaction. Fig. 10 shows that M_n increases linearly with conversion, up to approx. 80%. whilst PDI remains narrow for reaction with [MMA]:[3] - 200. In this case the expected M_n (theory) at 100% conversion = $[100/1 \times 100.14 \text{ (mass of MMA)}] + 220 \text{ (mass of end groups)} = 20248$. The PDI is broader than would be expected for a true living polymerisation with fast initiation (theoretically $1 + 1/DP$). However, PDI does not increase with increasing conversion as would be expected for a reaction with significant termination and this is most probably due to slow initiation relative to propagation.

In summary atom transfer polymerisation with the copper complex as catalyst and 3 as initiator leads to ω -hydroxy functional PMMA. The presence of the hydroxy group during the polymerisation does not reduce the control over the polymerisation, and a narrow PDI polymer with controlled M_n is obtained. The reaction shows all the characteristics of a living/pseudo living polymerisation. The structure of the product has been confirmed by MALDI-TOF-MS and NMR spectrometry. Furthermore the hydroxy functionality can be further functionalised by reaction with acid chlorides in a quantitative reaction.

Reaction ^d	[3]/ 10 ⁴ mol	[MMA]/ mol	t/min	Conver- sion (%) ^d	Mn SEC	PDI SEC
A ^b	9.61	0.187	70	-	2530	1.10
B ^c	9.72	0.047	120	-	4540 ^e	1.22 ^e
C ^c	9.72	0.047	120	-	3130	1.22
D ^b	9.61	0.187	60	0.21	-	-
E ^b	9.61	0.187	120	2.27	-	-
F ^b	9.61	0.187	180	15.74	4980	1.21
G ^b	9.61	0.187	240	48.20	12330	1.26
H ^b	9.61	0.187	300	59.75	15580	1.29
I ^b	9.61	0.187	360	66.18	17920	1.27
J ^b	9.61	0.187	420	72.11	19500	1.27
K ^b	9.61	0.187	480	75.05	20100	1.28
L ^b	9.61	0.187	480	-	19427 ^e	1.31 ^e

^a All reactions carried out with [2]:[CuBr]:[3] = 3:1:1. ^b 20 ml MMA in 40 ml xylene, ^c 5 mls MMA in 6 ml xylene. ^d From gravimetry. ^e After precipitation, otherwise as taken from reaction flask.

Further Examples of Initiators and Ligands

In order to demonstrate the effectiveness of the catalysts across the range of compounds chained, further experimentation was carried out.

5 Typical Polymerisation procedure

Methyl methacrylate (Aldrich) and xylene (AR grade, Fischer Scientific) were purged with nitrogen for 2 hours prior to use. The initiator, ethyl-2-bromoisobutyrate (98% Aldrich), and CuBr (99.999%, Aldrich) were used as obtained and 2-pyridinal π -alkylimines were prepared as above. A
10 typical reaction method follows. CuBr (0.134g, [Cu]:[Initiator]=1:1) was placed in a pre-dried Schlenk flask which was evacuated and then flushed with nitrogen three times. Methyl methacrylate (10ml) followed by 2-pyridinal π -alkylimine ([ligand]:[Cu]=2:1) was added with stirring and, within a few seconds, a deep, brown solution formed. Xylene (20ml) and,
15 if appropriate, inhibitor were then added and the flask heated in a thermostat controlled oil bath to 90°C. When the solution had equilibrated ethyl-2-bromoisobutyrate (0.14ml, [Monomer]:[Initiator]=100:1) was added. Samples were taken by pipette at certain times or the reaction followed by automated dilatometry. This apparatus consists of a glass
20 capillary tube that is set on top of a reaction vessel. The vessel is charged with a complete reaction mixture that has been freeze-pump-thaw degassed

to ensure no dissolved gases are released into the capillary. After the vessel is fitted, the capillary is filled with degassed solvent and the reaction mixture heated to the required temperature. During polymerisation monomer is converted to polymer with a decrease in the volume of the mixture. This decrease in volume can be followed by watching the meniscus fall in the capillary, a process done in this case by an electronic eye controlled by a computer program.

Characterisation of Polymers

Monomer conversion was calculated by gravimetry and/or ^1H NMR and the molecular weights and molecular weight distributions (polydispersities) found by gel permeation chromatography using tetrahydrofuran as eluent and the following columns (Polymer Laboratories): $5\mu\text{m}$ guard and mixed-E (3000x7.5mm), calibrated with PL narrow molecular weight poly(methyl methacrylate) standards with differential refractive index detection and/or UV.

Exp.	Initiator Formula	Ligand Formula	Amount ligand/g	Solvent (conc wt%)	Amt. CuBr	Amt. Initiator/ mL	Temp. °C	Time mins.
1	15	28	0.375	50	0.134	0.181	90	210
2	15	28	0.375	50	0.134	0.181	90	360
3	15	29	0.37	100	0.134	0.156	40	1440
4	15	33	0.273	33.3	0.134	0.137	90	240
5	15	40	0.273	33.3	0.134	0.137	90	1200
6	15	39	0.273	33.3	0.134	0.137	90	1320
7	15	44	0.25	33.3	0.134	0.137	90	2580
8	15	46	0.600	33.3	0.134	0.137	90	2580
9	15	32	0.610	33.3	0.134	0.137	90	300
10	15	49	0.423	33.3	0.134	0.137	90	1200
11	15	29	0.494	33.3	0.134	0.137	88	290
12	15	29	0.494	33.3	0.134	0.137	88	1260
13	15	31	0.536	33.3	0.134	0.137	90	1137
14	15	41	0.590	50	0.134	0.130	90	120
15	15	42	0.590	50	0.134	0.130	90	120
16	15	41	0.590	50	0.134	0.130	90	240
17	15	47	0.42	50	0.13	0.14	40	1050
18	15	47	0.42	50	0.13	0.14	40	2505
19	15	34	0.358	36	0.134	0.137	90	150
20	15	35	0.386	36	0.134	0.137	90	150
21	15	36	0.414	36	0.134	0.137	90	150
22	15	37	0.442	36	0.134	0.137	90	150
23	15	38	0.70	36	0.134	0.137	90	150
24	21	28	0.37	33.3	0.13	0.16	90	300
25	21	33	0.41	50	0.13	0.16	90	120
26	22	33	0.41	33.3	0.13	0.52	90	240
27	21	33	0.41	33.3	0.13	0.08	90	240
28	21	33	0.41	33.3	0.13	0.05	90	240
29	21	32	0.37	100	0.134	0.156	40	1440
30	21	32	0.37	33.3	0.134	0.156	90	300
31	23	29	0.37	33.3	0.134	0.178	90	270
32	23	29	0.37	33.3	0.134	0.178	90	1320
33	16B	29	0.37	33.3	0.134	0.193	90	1320
34	16B	45	0.45g	50	0.13	0.19	90	2760
35	23	45	0.45g	50	0.13	0.19	90	2760
36	16B	29	0.185	33.3*	0.067	0.096	90	2880

40* 25 mL of MMA

Results

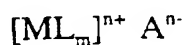
Exp.	Mn	PDI	%Conversion
1	10818	1.28	100
2	5060	1.34	13.5
3	12310	1.70	91.6
4	9198	1.19	66
5	8717	1.49	87
6	31666	1.65	49
7	9054	2.71	2
8	5250	1.63	2
9	21318	1.78	86
10	53395	1.72	39
11	8990	1.16	55.6
12	15147	1.26	97.6
13	8710	1.36	47.1
14	4300	1.45	5
15	4700	1.65	10
16	6200	1.45	28
17	6577	1.27	47
18	11216	1.23	75
19	6500	1.18	60.0
20	7400	1.20	68.3
21	7320	1.20	72.1
22	7580	1.20	73.4
23	7900	1.23	73.4
24	11710	1.30	
25	28314	1.19	
26	7700	1.14	
27	28330	1.15	68.5
28	36380	1.17	50.6
29	23780	1.07	38.5
30	26640	1.17	52.52
31	2177	1.10	
	2135 (by NMR)		
32	1000	1.11	3.8
33	1900	1.08	20.3
34	11009	1.08	
35	10200	1.13	
36	23700	1.13	

CLAIMS

- 5 1. A catalyst for addition polymerisation of olefinically unsaturated monomers comprising:
- a) A first compound
- MY
- 10 where: M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand.
- Y is a monovalent divalent or polyvalent counterion:
- 15 b) An initiator compound comprising a homolytically cleavable bond with a halogen atom: and
- c) An organodiimine. where at least one of the nitrogens of the diimine is not part of an aromatic ring.
- 20
2. A catalyst for addition polymerisation of olefinically unsaturated

monomers comprising:

d) A first component of Formula



5

where: M = a transition metal of low valency state

L = an organodiimine where at least one of the nitrogens of the diimine is not a part of an aromatic ring.

A = an anion

10

n = an integer of 1 to 3

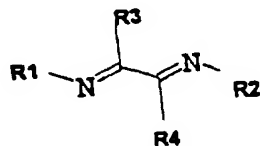
m = an integer of 1 to 2, and

e) An initiator compound comprising a homolytically cleavable bond with a halogen atom.

15

3. A catalyst according to any previous claim wherein the organodiimine is selected from:

a 1,4-diaza-1,3-butadiene

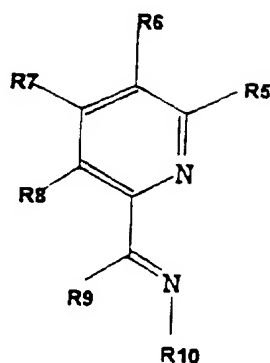


20

Formula 24

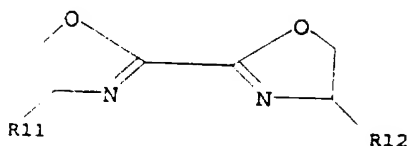
46

a 2-pyridine carbaldehyde imine



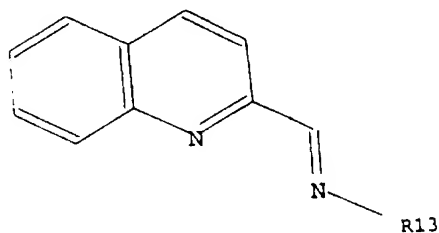
Formula 25

an oxazolidone



Formula 26

or a quinoline carbaldehyde



Formula 27

where:

R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} are independently selectable and may be selected from H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl, CH_2 Ar (where Ar is aryl or substituted) or a halogen;

R₃ to R₉ are independently selectable and may be selected from H, straight chain, branched chain or cyclic alkyl, hydroxyalkyl, carboxyalkyl, aryl, CH₂ Ar, a halogen, OCH_{2n+1} (where n is an integer of 1 to 20), NO₂, CN, O = CR (where R = alkyl, aryl, substituted aryl, benzyl PhCH₂ or a substituted benzyl).

4. A catalyst according to claim 3 wherein R₁ to R₁₃ are selected from C₁ to C₂₀ alkyl, C₁ to C₂₀ hydroxyalkyl, C₁ to C₂₀ carboxyalkyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyldecyl or lauryl.

5. A catalyst according to claim 3 or claim 4, wherein the organodiimine comprises a chiral centre.

6. A catalyst according to claims 3 to 5 wherein one or more adjacent R₁ and R₃, R₃ and R₄, R₄ and R₂, R₁₀ and R₉, R₈ and R₉, R₈ and R₇, R₇ and R₆, R₆ and R₅ groups are selected from alkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, containing 5 to 8 carbon atoms.

7. A catalyst according to any previous claim wherein M is selected from Cu(I), Fe(II), Co(II), Ru(II), Ni(II) Sm(II), Ag(I) and Yb(II).

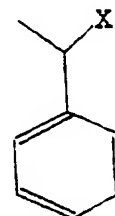
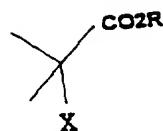
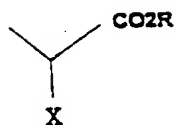
8. A catalyst according to any of claims 1 and 3 to 7, wherein Y is selected from Cl, Br, I, NO₃, PF₆, BF₄, SO₄ and CF₃ SO₃, CN, SPh, ScN and SePh.

9. A catalyst according to any of claims 2 to 7 wherein A is selected from Cl, Br, F, I, NO₃, SO₄ and CuX₂ (where X is a halogen).

10. A catalyst according to any previous claim, wherein the initiator is selected from:

RX

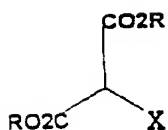
Formula 2



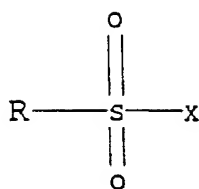
Formula 3

Formula 4

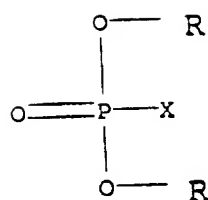
Formula 5



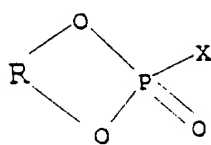
Formula 6



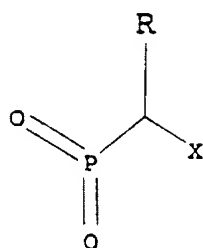
Formula 7



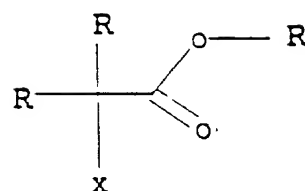
Formula 8



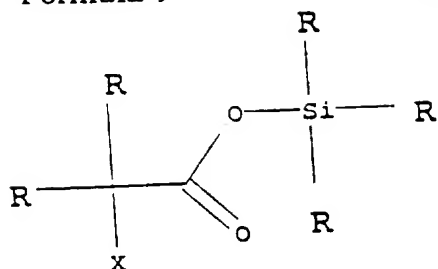
Formula 9



Formula 10



Formula 11

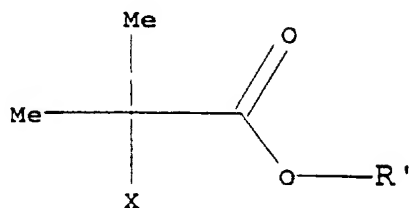


Formula 12

15 where R is independently selectable and is selected from straight chain alkyl, branched chain alkyl, cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl, aryl and substituted aryl and substituted benzyl.

X = a halide

11. A catalyst according to claim 10, wherein the initiator is



where:

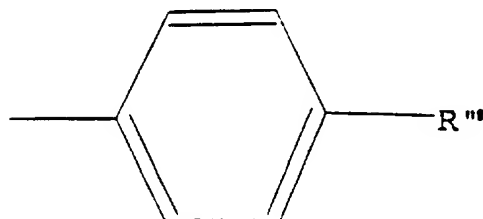
X = Br, I or Cl, preferably Br

R' = -H,

$-(CH_2)_pR''$ (where p is a whole number and $R'' = H, OH,$

$NH_2, SO_3H, COOH,$ halide, $COX,$ where X is Br, I or Cl),

or



$R''' = -COOH, -COX$ (where X is Br, I or Cl), $-OH, -NH_2$ or $-SO_3H$

12. A catalyst according to claim 11 wherein b is 2-hydroxyethyl-2' bromopropionate.

13. The use of a catalyst according to any previous claim in the

addition polymerisation of one or more olefinically saturated monomers.

14. The use of a catalyst according to claim 13 at a temperature between -20°C to 200°C.

5

15. The use of a catalyst according to claim 14 between 20°C and 130°C.

16. The use of a catalyst according to claims 13 to 15, wherein the
10 olefinically saturated monomer is selected from methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl
15 methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates; methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene, α -methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula
20 $\text{CH}_2 = \text{C}(\text{Hal})_2$ where each halogen is independently Cl or F; optionally substituted butadienes of the formula $\text{CH}_2 = \text{C}(\text{R}^{15}) \text{C}(\text{R}^{15}) = \text{CH}_2$ where

R^{15} is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula $CH_2 = CHSO_2OM$ wherein M is Na, K, Li, $N(R^{16})_4$, R^{16} , or $-(CH_2)_2-D$ where each R^{16} is independently H or C1 or C10 alkyl, D is CO_2Z , OH, $N(R^{16})_2$ or SO_2OZ and Z is H, Li, Na, K or $N(R^{16})_4$; acrylamide or derivatives thereof of formula $CH_2 = CHCON(R^{16})_2$, and methacrylamide or derivatives thereof of formula $CH_2 = C(CH_3)CON(R^{16})_2$. Mixtures of such monomers may be used.

17. The use of a catalyst, as defined in claims 1 and 3 to 12, according to claims 13 to 16, wherein the ratio (c):(a) is 0.01 to 1000 and the ratio of (a):(b) is 0.0001 to 1000.

18. The use of a catalyst as defined in claims 2 to 12 according to claims 13 to 16 wherein the ratio of M:initiator is between 3:1 and 1:100.

19. The use of catalyst according to claims 13 to 16, where the polymerisation is undertaken in water, a protic or non-protic solvent.

20. The use of a catalyst according to claims 1 to 12 to produce a statistical copolymer, a block copolymer, a telechelic polymer or a comb and graft copolymer of monomers according to previous claim.

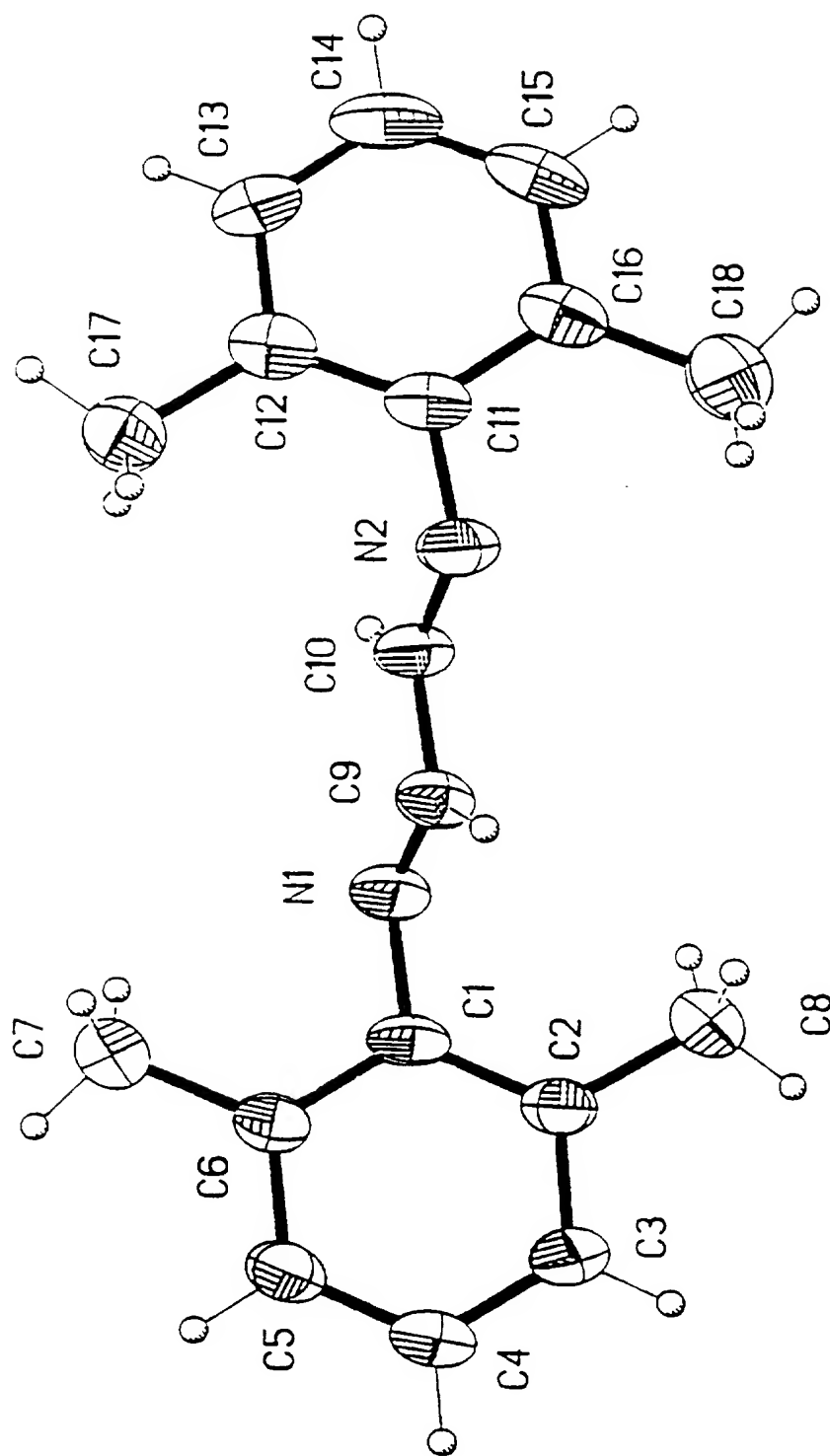


Figure 1

2/9

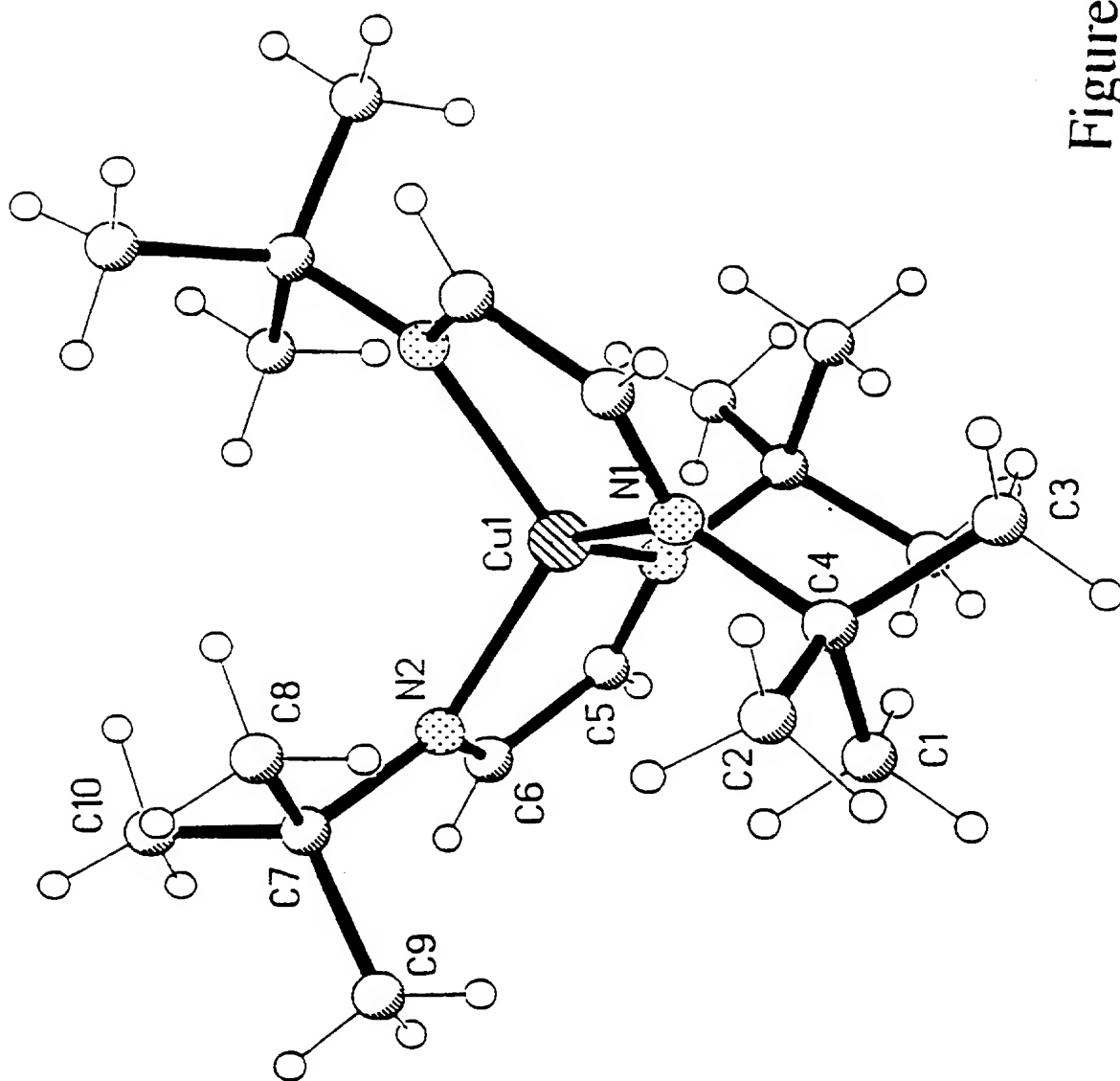


Figure 2

3/9

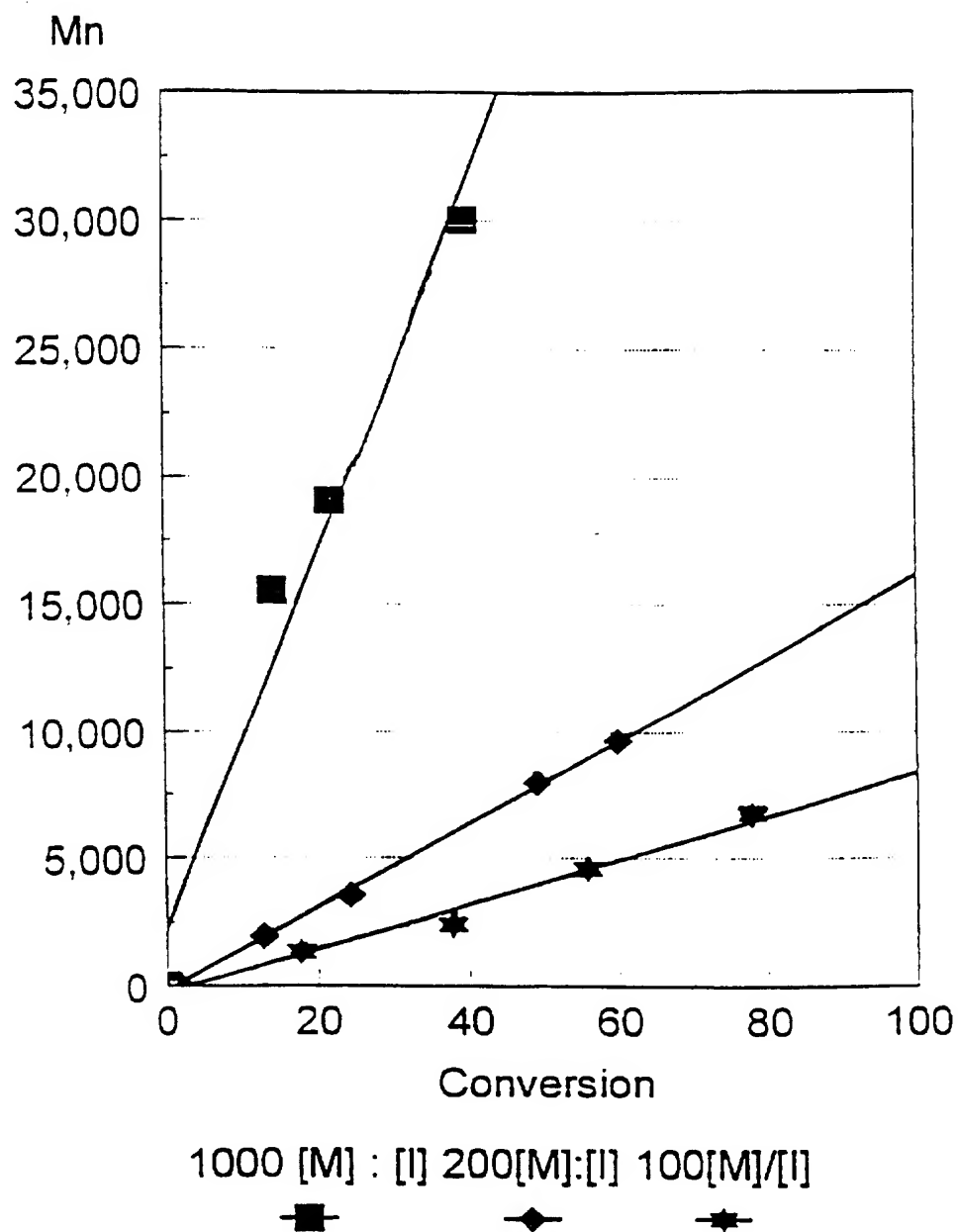


Figure 3

4/9

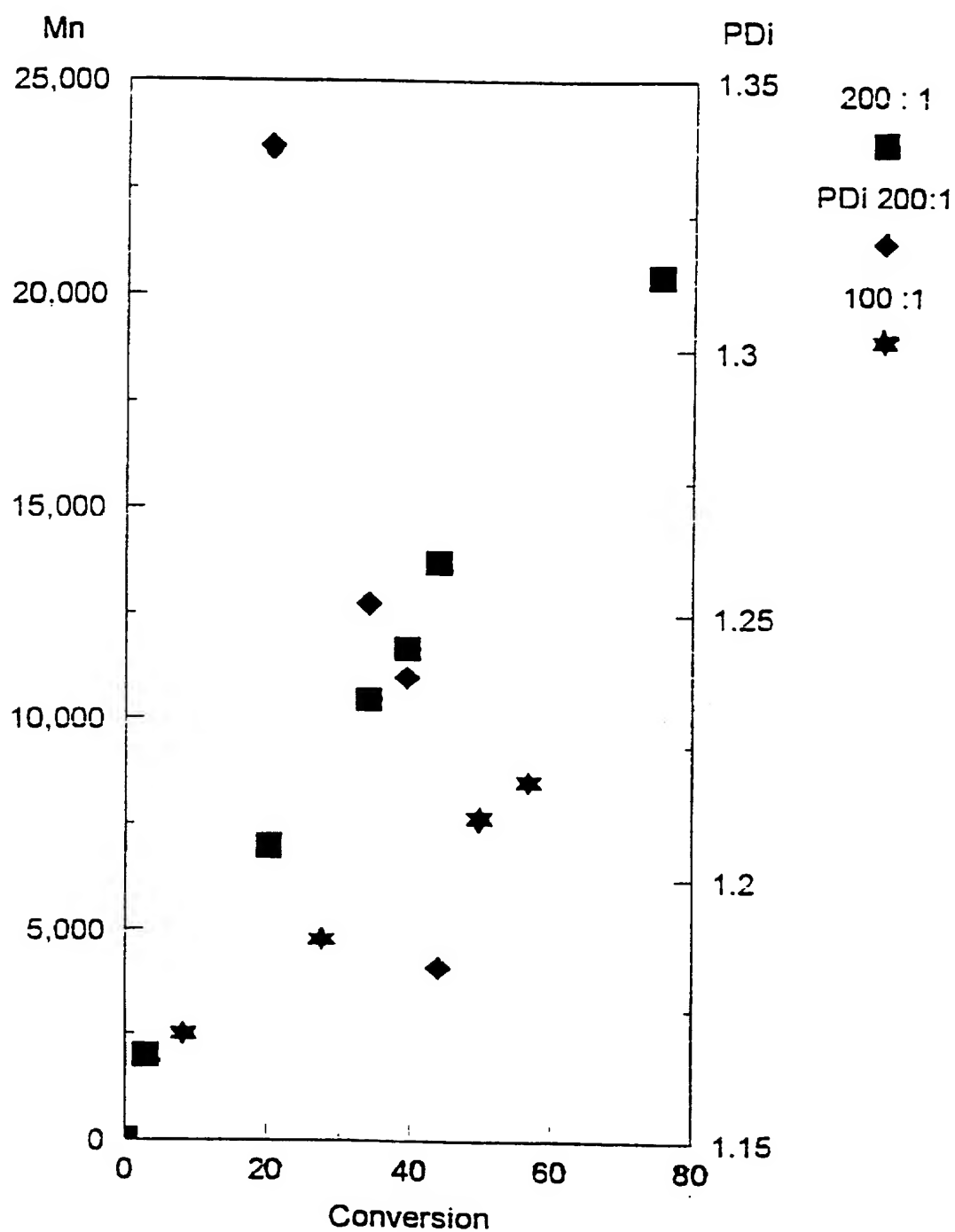


Figure 4

5/9

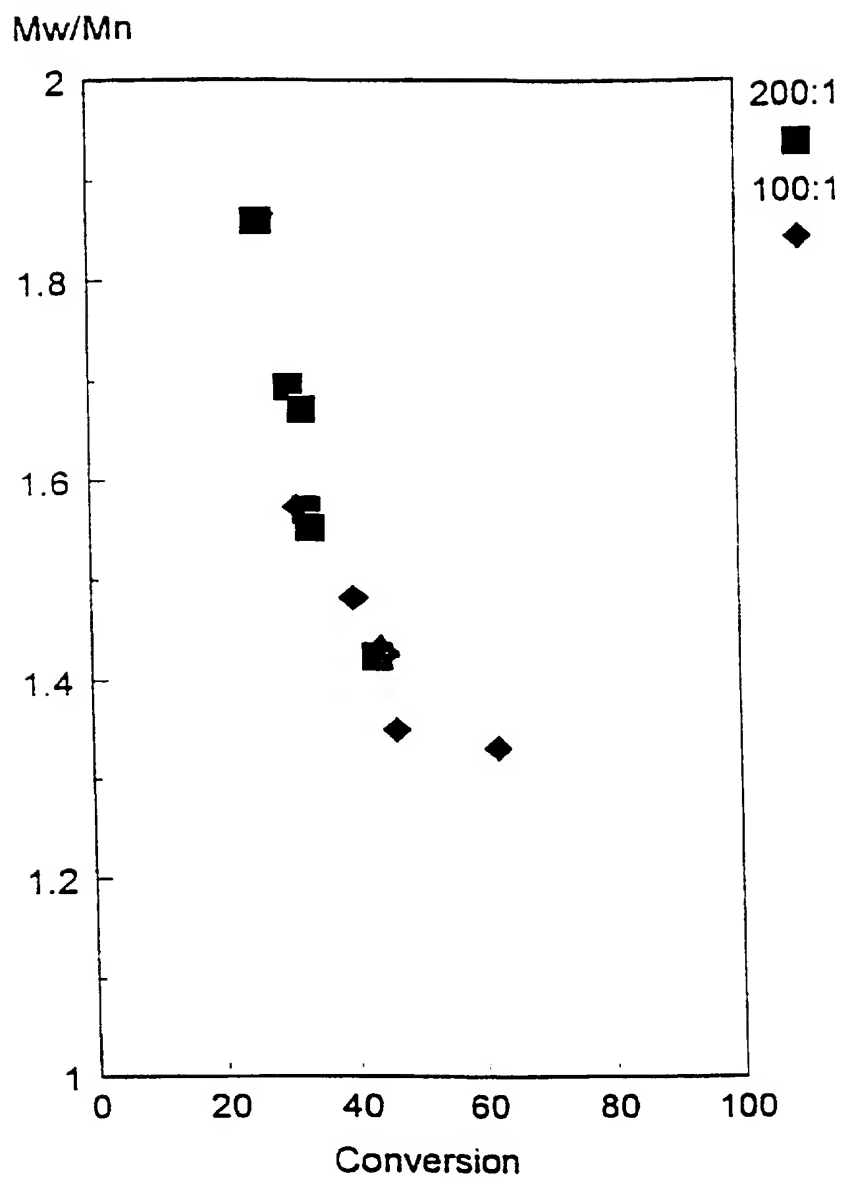


Figure 5

6/9

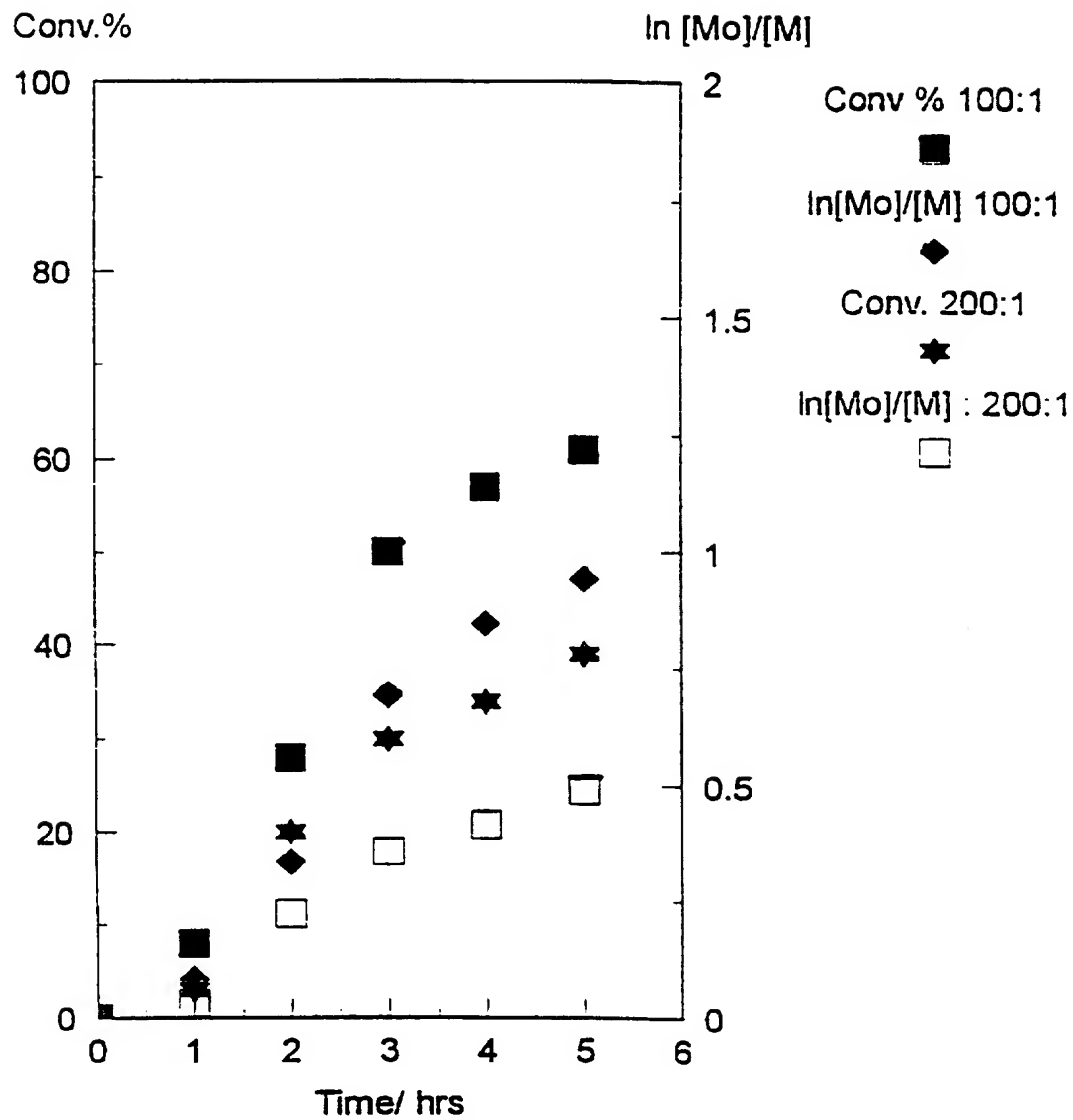


Figure 6

7/9

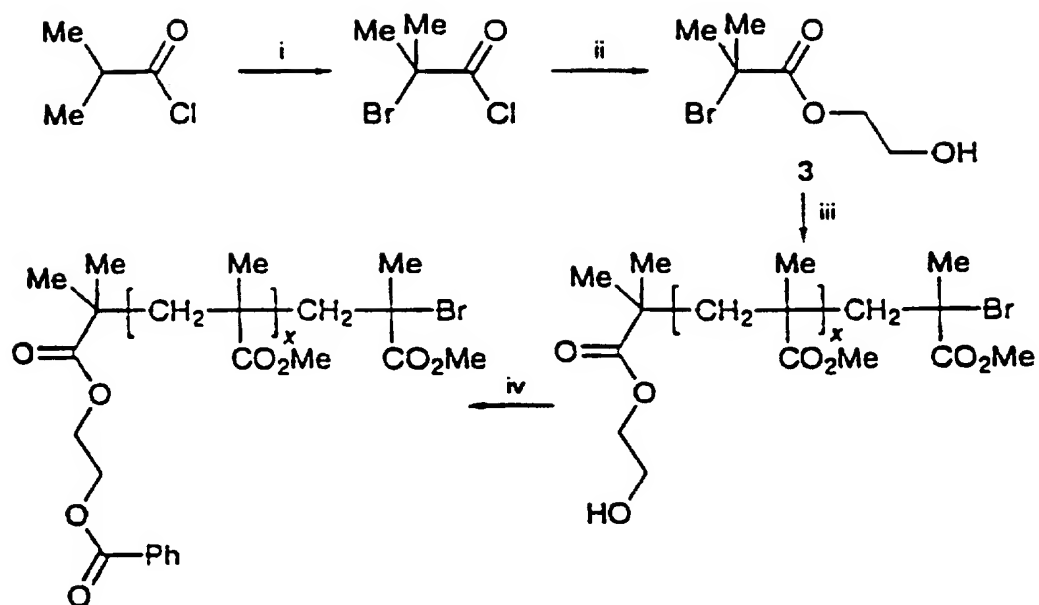


Figure 7

8/9

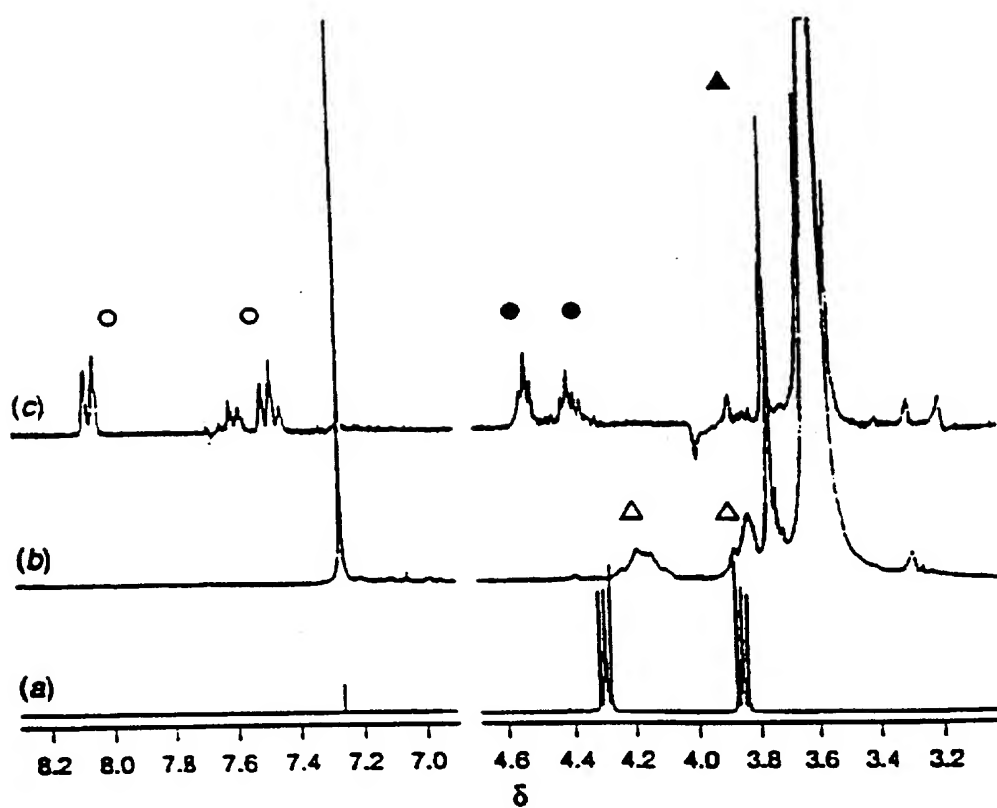


Figure 8

9/9

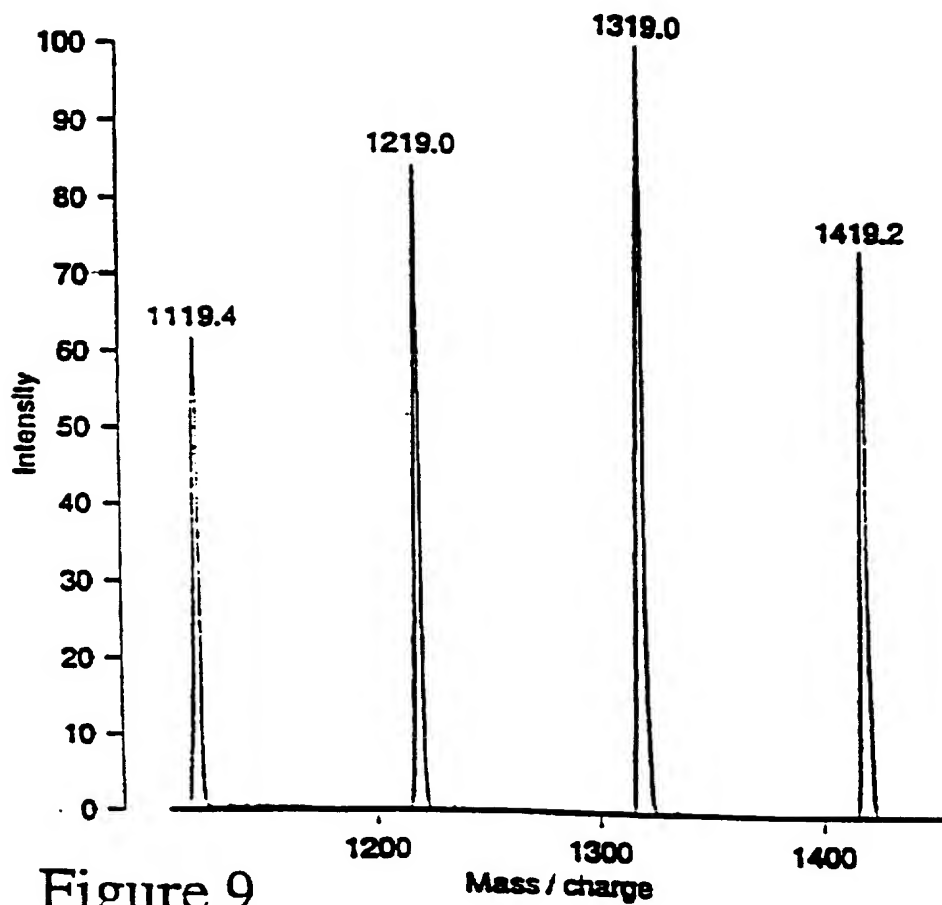


Figure 9

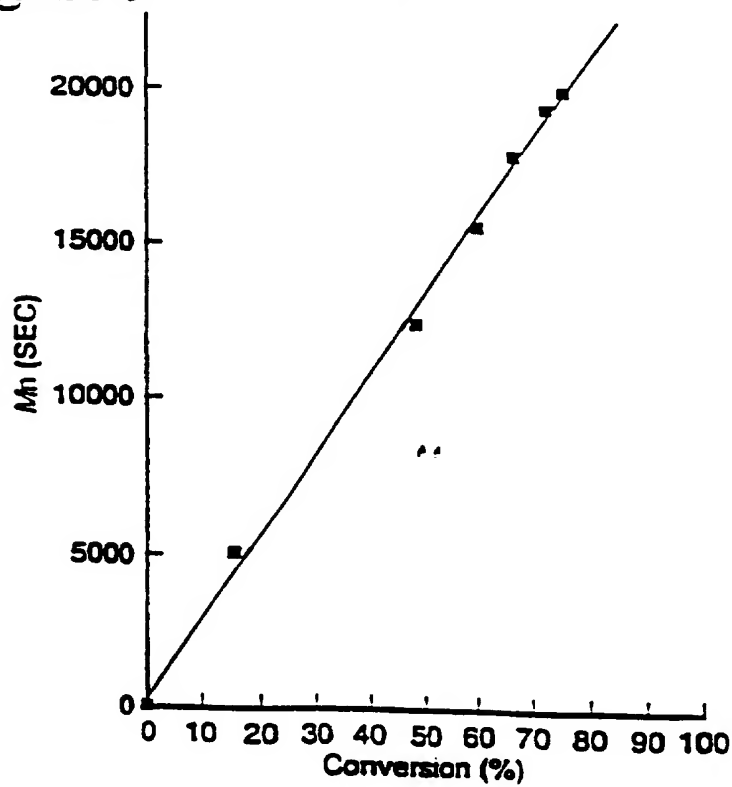


Figure 10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/01589

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/10 C08F4/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SVOBODA M ET AL: "DIAZADIEN-NICKEL-ALKYLE" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 191, 1 January 1980, pages 321-328, XP000590806 see abstract see page 322, line 38 - page 323, line 8 see page 327, paragraph 4 ---	1
A	KOTEN VAN G ET AL: "1,4-DIAZA-1,3-BUTADIENE (ALPHA-DIIMINE) LIGANDS: THEIR COORDINATION MODES AND THE REACTIVITY OF THEIR METAL COMPLEXES" ADVANCES IN ORGANOMETALLIC CHEMISTRY, vol. 21, 1 January 1982, STONE F G A;WEST R, pages 151-239, XP000576172 see page 233, paragraph 2 - paragraph 5 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

Date of the actual completion of the international search

4 November 1997

Date of mailing of the international search report

19. 11. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fischer, B